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Flame-retardant plant thermoplastics directly prepared by single ionic liquid substitution

Ryunosuke Nishita[1], *Kosuke Kuroda*[*,1], *Shiori Suzuki*[1], *Kazuaki Ninomiya*[2], *and Kenji Takahashi*[1]

[1] Faculty of Biological Science and Technology, Institute of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

[2]Institute for Frontier Science Initiative, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

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ABSTRACT

Grass and wood biomass (bagasse, cedar, and eucalyptus) were directly converted to flame-retardant thermoplastics by dissolution in an ionic liquid mixture and successive precipitation. During dissolution, the hydroxy groups of the biomass were substituted with a phosphonate-type ionic liquid. The three resulting biomass samples were formed into thin films by hot pressing at 140–160 °C. They also self-extinguished a fire by forming foamed char layers after contacting the fire of an alcohol lamp. In this method, more than 86% of the hydroxy groups were maintained after ionic liquid substitution because the single phosphonate-type ionic liquid acted as a plasticizer and flame retardant in the plant biomass. Therefore, the plant biomass-derived flame-retardant thermoplastics have the potential for further functionalization.

KEYWORDS

Flame retardancy / thermoplasticity / ionic liquid / biomass / cellulose / hemicellulose / lignin

INTRODUCTION

A large amount of plant biomass has been produced as waste (e.g., bagasse and sawdust) in the industrial processes of food and manufacturing products, and the biomass has attracted attention as renewable resources. However, utilization of the biomass resources is quite difficult through chemical modification because of poor solubility of the plant biomass. In most cases, plant biomass has been used after separation and refinement to each pure component: cellulose, hemicellulose, and lignin. Cellulose utilization has especially progressed over the past decades, and for example, cellulose has been converted to thermoplastics by acylation.[1-4] Flame-retardancy is also important when using cellulose thermoplastics for daily use because these are flammable. Aoki *et al.* have reported a flame-retardant cellulose thermoplastic by adduction of a phosphoric acid-type flame retardant to the residual hydroxy groups of cellulose propionate (CP).[5]

On the other hand, we have reported flame-retardant cellulose thermoplastics just by dissolution in a single ionic liquid (salts that are liquid below 100 °C) species (hemicellulose and lignin have been also thermoplasticized with flame retardancy) and precipitation.[6] Specifically, the anion of 1-ethyl-3-methylimidazolium methylphosphonate ($[C_2mim][(MeO)(H)PO_2]$)[7, 8] is covalently introduced into the hydroxy group of cellulose, hemicellulose, or lignin simply by mixing and heating at a high temperature. As a result, this method adds thermoplasticity and flame-retardancy, which are intrinsic effects of typical ionic liquids[9-11], to the samples and prevented bleeding out of the ionic

liquid by covalent bonding. Furthermore, we have found that an ionic liquid combining a dialkylimidazolium cation and phosphonate anions acts as an intumescent flame retardant.[6] The intumescent flame retardant releases inert gases, such as N_2, when forming char by phosphorus compounds, resulting in foamed char layers. These foamed char layers are highly adiabatic, and thus the cellulose, hemicellulose, and lignin which are substituted with $[C_2mim][(MeO)(H)PO_2]$ (IL-cellulose, IL-hemicellulose, and IL-lignin) are able to self-extinguish.[6] There is an additional significant advantage to this method as follows. In the method reported by Aoki et al. (introducing a phosphate-type flame retardant to CP)[5], the resulting samples cannot be further functionalized because almost all hydroxy groups are substituted by the flame-retardant- and plasticizer-groups: there are no more reactive groups in the polymers. Therefore, further control of other properties of the cellulosic plastics that are important for molding and practical use (e.g. physico-chemical properties, such as viscosity and solubility, and mechanical properties, such as bending strength, tensile strength, and elastic modulus) cannot be achieved. On the other hand, more than 66% of the unreacted hydroxy groups are maintained in this method mentioned above, suggesting potential for further functionalization to control the above properties.[7]

From these results, flame retardant thermoplastics from each component of biomass—cellulose, hemicellulose, and lignin—are ready to use. However, complicated purification is required to obtain each component from the plant biomass. In addition, all components cannot be recovered

with high purities and yields. For example, an alkaline treatment followed by bleaching to extract pure cellulose causes denaturation and decomposition of lignin[12] and may cause decomposition of carbohydrates.[13] Thus, it is preferable to prepare the flame-retardant thermoplastics directly from the plant biomass, based on the effort, time, cost, and yield. Therefore, in this study, flame retardancy and thermoplasticity were added to the plant biomass without separation and purification. The poor solubility of the plant biomass is here problematic. Plasticization of wood through heterogeneous reactions has been reported,[14, 15] and a homogeneous reaction is preferable for obtaining homogeneous plant-derived plastics because plant cell walls have a heterogeneous hierarchical structure. Specific solvents, such as dimethyl sulfoxide (DMSO)/LiCl and DMSO/tetrabutylammonium fluoride, dissolve wood; however, they require ball-milling as a pretreatment.[16, 17] On the other hand, ionic liquids have been reported to dissolve plant biomass without any pretreatment.[18-21] Therefore, it is expected that the hydroxy group of plant biomass can be substituted to $[C_2mim][(MeO)(H)PO_2]$ as well as cellulose, i.e., only by mixing $[C_2mim][(MeO)(H)PO_2]$ and plant biomass while heating and can be used as flame-retardant thermoplastics.

The low thermal fluidity of plant biomass is a concern when making flame-retardant thermoplastics from plant biomass. Plant biomass does not exhibit fluidity even at high temperature because of three factors. The first factor is the high crystallinity of cellulose.[22] The softening point

can be decreased by destroying the hydrogen bonding network between the cellulose chains because of the high hydrogen bonding ability of the ionic liquids.[9] Furthermore, the softening point can also be decreased by substituting the hydroxy groups with [(MeO)(H)PO_2] anions because the substitution decreases the number of hydroxy groups. The effectiveness of this strategy has been proven because IL-cellulose shows fluidity at an intermediate temperature.[6] For the second factor, a certain amount of lignin in the plant biomass chemically bonds with hemicellulose and forms a large macromolecule referred to as the lignin carbohydrate complex (LCC).[23] The third factor is the high branching of lignin.[24, 25] Regarding to these factors, we have reported that the LCC and lignin are partially cleaved in [C_2mim][(MeO)(H)PO_2] and a similar ionic liquid at approximately 120 °C.[26, 27] Because the substitution with [C_2mim][(MeO)(H)PO_2] is conducted at a high temperature of 160 °C, the partial cleavage of LCC and lignin could simultaneously occur. In this study, the direct preparation of flame-retardant thermoplastics was attempted by adducting [C_2mim][(MeO)(H)PO_2] to the plant biomass by mixing at 160 °C based on these hypotheses. This method further enables the development of flame-retardant plant thermoplastics with a low substitution ratio because [C_2mim][(MeO)(H)PO_2] acts as a plasticizer and flame retardant as well as IL-cellulose. It makes room for further functionalization for molding and practical use as mentioned above. To the best of our knowledge, this is the first study on the direct preparation of a flame-retardant thermoplastic from plant biomass without pretreatments.

EXPERIMENTAL PROCEDURE

Materials

Bagasse, Japanese cedar, and eucalyptus (Sanwa Ceruciron Co., Ltd., Yokkaichi, Japan) were purchased and used with a particle size of 250–500 μm. 1-Ethyl-3-methylimidazolium acetate ([C_2mim]OAc) (purity: ≥ 95%, Iolitec Ionic Liquids Technologies GmbH, Heilbronn, Germany) was purchased and used after drying. Dichloromethane, DMSO, and isopropenyl acetate (Sigma-Aldrich Co., LLC., St. Louis, MO, USA) were purchased and used as received. Acetone (Kanto Chemical Co. Inc., Tokyo, Japan) was purchased and used as received. [C_2mim][(MeO)(H)PO_2] (purity: ≥ 97%, Kanto Chemical Co. Inc., Tokyo, Japan) was purchased and used after drying. A dialysis membrane (MWCO 1000) (Funakoshi Co. Ltd., Tokyo, Japan) was purchased and used as received. Triethyl phosphate and vinyl decanoate (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) were purchased and used as received. Cellulose propionate (Scientific Polymer Products, Inc., New York, USA) was purchased and used as received. Filter paper (No. 5C) derived from cellulose (Advantec, Co., Ltd., Tokyo, Japan) was purchased and used as received.

Synthesis of [C_2mim][(MeO)(H)PO_2]-substituted plant biomass (IL-bagasse, IL-cedar, and IL-eucalyptus)

The introduction of [C_2mim][(MeO)(H)PO_2] to the plant biomass was conducted based on

previous reports[6, 28]; however, [C_2mim]OAc was added in order to improve the biomass solubility (a detailed explanation is provided in the results and discussion). Bagasse, Japanese cedar, and eucalyptus (0.5 g) were respectively added in [C_2mim]OAc (5.0 g). The biomass was dissolved by heating at 120 °C for 2 h. Then, 5.0 g of [C_2mim][(MeO)(H)PO_2] was added and heated to 160 °C for 3 h under an Ar atmosphere. Water (20 mL) was added to the resulting samples, and the unreacted ionic liquids were removed by dialysis for 48 h (water was exchanged every 8 h) with 500 mL of water. After filtration, the filtrates were dried *in vacuo* (IL-bagasse: 0.28 g, IL-cedar: 0.26 g, IL-eucalyptus: 0.26 g from 0.50 g of each raw biomass as final yields). The [C_2mim][(MeO)(H)PO_2]-substituted biomasses were referred to as IL-bagasse, IL-cedar, and IL-eucalyptus, in this study.

The structures of the IL-bagasse, IL-cedar, and IL-eucalyptus were confirmed by ^{1}H NMR in DMSO-d_6 at room temperature (ECA-600, JEOL, Ltd., Tokyo, Japan), while the measurement was conducted with a soluble part, and FT-IR (NICOLETis10, Thermo Fisher Scientific, K.K., Tokyo, Japan). The removal of the unreacted IL was also by ^{1}H NMR. The signals attributed to unreacted [C_2mim][(MeO)(H)PO_2], especially sharp P-*H* and P-CH_3, were not observed. The substitution ratios of the hydroxy groups of the plant biomass with [C_2mim][(MeO)(H)PO_2] were measured by ^{31}P NMR (ECA-600, JEOL, Ltd., Tokyo, Japan). Triethyl phosphate was added as a standard for quantification. Each substitution ratio in mol of IL-bagasse, IL-cedar, and IL-eucalyptus was estimated from the results of ^{31}P NMR and the amount of hydroxy group included in the plant biomass species. The

amount of hydroxy groups in the plant biomass was calculated from the content of cellulose, hemicellulose, and lignin determined by the NREL method[29] and the number of hydroxy groups of each component (e.g., three hydroxy groups in one anhydroglucose unit). The hydroxy group content of lignin was 4.26 mmol/g measured using a method described in previous literatures[6, 29]. Alkali lignin was used as the model lignin to estimate the hydroxy group content.

We tried gel permeation chromatography measurement of the samples to check possible degradation of polymers but it was impossible, at least with our systems, because of poor solubilities of raw- and IL-biomasses. We were able to subject only IL-lignin to gel permeation chromatography and the molecular weight shifted to high molecular weight by adduction of $[C_2mim][(MeO)(H)PO_2]$, compared to unreacted alkali lignin (Fig. S1). We can describe “lignin is still polymer” but cannot describe about polysaccharides. We neither can describe “alkali lignin does not decompose at all” because we conducted dialysis for purification and alkali lignin is different from native lignin. The gel permeation chromatography (Prominence UFLC system, Shimadzu Co., Kyoto, Japan) was conducted with polystyrene standards using TSK gel α-M (Tosoh Co., Tokyo, Japan). LiBr (0.01 mol L^{-1}) in dimethylformamide (HPLC grade, Kanto Chemicals Co., Inc., Tokyo, Japan) was used as an eluent (flow rate: 1.0 mL min^{-1}) at 40 °C.

Synthesis of bagasse acetate decanoate

Bagasse acetate decanoate was synthesized for comparison with the IL-biomass samples. Two different types of acyl groups were introduced because mixing long- and short- alkyl-chains significantly decreases the apparent melting point. Bagasse was successively decanoylated and acetylated in [C_2mim]OAc/DMSO, referring to the literature.[30] The synthetic procedures are briefly described below.

Bagasse (3.0 g), [C_2mim]OAc (50 g), and DMSO (75 mL) were mixed under an Ar atmosphere. The obtained solution was stirred at 110 °C for 16 h. After cooling the solution to 80 °C, a small amount of vinyl decanoate (2.1 mL) and an excess amount of isopropenyl acetate (100 mL) were added to the solution in order, and each reaction was conducted for 30 min. The substitution ratio was 97% (acetyl group: 68%, decanoyl group: 29%).

Evaluation of thermoplasticity

To evaluate the thermoplasticity of the IL-biomass samples, the minimum film-forming temperature was used, defined as the temperature at which two overlapped sample films were pressed at 45 kN using a hot press (Imoto Machinery Co., Ltd., Kyoto, Japan) and could be molded into one sheet cleanly. The minimum film-forming temperature was investigated by increasing by 10 °C increments from 80 °C. The thermal decomposition temperature was evaluated by a thermogravimetric analysis (TGA) (DTG-60AH, Shimadzu Co., Kyoto, Japan) under air (10 °C/min). Differential scanning

calorimetry (DSC) (DSC 60A plus, Shimadzu Co., Kyoto, Japan) was conducted with a heating scan rate of 10 °C/min from 30 to 170 °C.

Evaluation of the flame retardancy

The quantitative flame-retardancy was evaluated by the residual weight in the TGA under nitrogen and air. In addition, the combustion behavior of the samples was observed using an alcohol lamp.

RESULTS AND DISCUSSION

Bagasse (grass), Japanese cedar (softwood), and eucalyptus (hardwood), which are known to be produced as waste in manufacturing processes, were used as the samples of plant biomass. The biomass samples used in this study were prepared simply by cutting/crushing with a mixer but without intense pretreatments such as ball-milling: these samples are similar to real waste such as roughly crushed bagasse and sawdust. The use of the fine biomass waste has been faced to limitation, while large wood stuffs are used as architectural materials. $[C_2mim][(MeO)(H)PO_2]$-substituted plant biomass was prepared similarly to IL-lignin as previously reported (lignin was dissolved in $[C_2mim][(MeO)(H)PO_2]$ at 160 °C and reacted for 3 h) [6]. However, IL-bagasse could not be obtained because the bagasse was not sufficiently dissolved in $[C_2mim][(MeO)(H)PO_2]$. Here, we focused on 1-ethyl-3-methylimidazolium acetate ($[C_2mim]OAc$), which has a better dissolution ability to the

plant biomass.[31, 32] Bagasse was stirred in [C_2mim]OAc at 120 °C for 2 h, and a large percentage of the bagasse was dissolved based on a visual confirmation. Then, [C_2mim][(MeO)(H)PO_2] was added as a co-solvent and reactant, which prevented precipitation because of its intermediate dissolution ability, and reacted at 160 °C for 3 h. IL-cedar and IL-eucalyptus were prepared using the same method.

In the ^{1}H NMR spectrum of a soluble part of IL-bagasse, peaks derived from [C_2mim] cations were observed at 1.37, 3.82, 4.16, 7.68, 7.77, and 9.23 ppm, while peaks derived from the [(MeO)(H)PO_2] anions were observed at 6.01 and 6.99 ppm (Fig. S2). Furthermore, the signal attributed to the methyl group of the [(“Me”O)(H)PO_2] anion (approximately 3.2 ppm) was not observed in the spectrum of IL-bagasse. These results suggest that the [(MeO)(H)PO_2] anion was covalently introduced into bagasse, accompanied by the removal of the methyl group of the [(“Me”O)(H)PO_2] anion. IL-cedar and IL-eucalyptus were also confirmed to have been synthesized as well as IL-bagasse (see Fig. S2). The introduction of [C_2mim][(MeO)(H)PO_2] into each plant biomass was also confirmed by FT-IR (Fig. S3). The peaks derived from the P-O-C bond at 821 cm^{-1}, P=O bond at 1211 cm^{-1}, and C=N bond at 1571 cm^{-1} were detected in the IL-bagasse, while these were not observed in the unreacted bagasse[33, 34]. The peaks derived from these bonds were also detected in IL-cedar and IL-eucalypts (see Fig. S3). The signals derived from P=O and C=N were observed at similar wavenumbers in [C_2mim][(MeO)(H)PO_2]; however, the signal from P-O-C was not observed at approximately 821 cm^{-1}. The signal at 744 cm^{-1} may be the corresponding signal because P-O-“C”

changed from the methyl group to the carbon atoms of the carbohydrates and lignin. These results indicated that [C_2mim][(MeO)(H)PO_2] was covalently introduced to each plant biomass.

The substitution ratio of the hydroxy groups of bagasse, cedar, and eucalyptus with [C_2mim][(MeO)(H)PO_2] was roughly estimated by ^{31}P NMR (spectra are shown in Fig. S4). Their substitution ratio was 13, 8, and 10 mol%, respectively, against the number of hydroxy groups. Because the substitution ratios of IL-cellulose, IL-xylan, and IL-lignin were 33, 32, and 14 mol%, respectively,[6] those of the IL-biomass samples were lower. This could be because of the lignin contained in plant biomass and the lower concentration of [C_2mim][(MeO)(H)PO_2] owing to dilution by [C_2mim]OAc used to dissolve the biomass. From these results, IL-bagasse, IL-cedar, and IL-eucalyptus maintained 87, 92, and 90 mol% of the hydroxy groups, respectively, after derivatization. Therefore, there is potential for further functionalization.

The thermal properties of the samples regarding thermoplasticity were investigated (Table 1). In this study, the film formation ability by hot press was evaluated as the thermoplasticity. The minimum film-forming temperatures were determined using a hot press machine, and those of IL-bagasse, IL-cedar, and IL-eucalyptus were 160, 140, and 140 °C. The resulting films shown in Fig. 2 were flexible. In addition, these films are brown color owing to containing lignin but transparent. It seems surprising that thermoplasticity was shown with only 10 mol% substitution ratio. Here, as an example, Chen *et al*. reported that mulberry wood shows thermoplasticity at 150 °C with ionic liquid

addition (i.e., just mixing) of less than 10 wt% against the weight of the biomass.[10] The substitution ratios of the samples, IL-bagasse, IL-cedar, and IL-eucalyptus (13, 8, 10 mol%, respectively), correspond to 28, 19, and 23 wt% of ionic liquid contents, respectively. Therefore, it is not surprising that the IL-biomass samples showed a film-forming temperature at 140–160 °C. On the other hand, the minimum film-forming temperature was approximately the same as that of the sample prepared by only mixing ionic liquid, although the ionic liquid contents in IL-biomass samples were approximately 2–3 times, compared to thermoplastics based on biomass/IL mixture. It is presumably based on the difference in the state of the ionic liquid, namely free or fixed.

The composition ratios of cellulose, hemicellulose, and lignin contained in the bagasse, cedar, and eucalyptus used this research are listed in Table S1. The minimum film-forming temperatures of IL-bagasse, IL-cedar, and IL-eucalyptus were calculated as 133, 136, and 134 °C, respectively, from the ratio of the biopolymer and the individual minimum film-forming temperature (IL-cellulose, IL-xylan, and IL-lignin: 100, 140, and 180 °C, respectively). The minimum film-forming temperature of all samples was over 140 °C, which was slightly higher than expected. The differences were attributed to the lower substitution ratio of the IL-biomass samples than that of IL-cellulose, IL-xylan, and IL-lignin. The composition of IL-cedar and IL-eucalyptus differed; however, both had a minimum film-forming temperature of 140 °C. This indicates that this method was not significantly affected by the biomass components. Conversely, the minimum film-forming

temperature of IL-bagasse was higher than that of IL-eucalyptus, although the composition ratio of the biopolymer was approximately the same. Because the substitution ratio of IL-bagasse was higher than IL-eucalyptus, other factors such as molecular weight of the components might cause the slight difference. However, considering that the minimum film-forming temperature of the native biomass species is much higher than the thermal decomposition temperature, the difference between 140 °C and 160 °C seems not to be large. To investigate further characteristics of the samples, the samples were subjected to DSC (Fig. S5). Some grass transition temperatures were observed but it is difficult to clarify the relations between the minimum film-forming temperatures and the grass transition temperatures because the biomasses are the intrinsically mixtures of polymers.

Plant biomass plastics synthesized by a heterogeneous reaction have a melting point of 140–320 °C.[14, 24, 25] In addition, the minimum film-forming temperature of bagasse acetate decanoate (substitution ratio: 97%) was 120 °C. It is known that the thermoforming temperature decreases by introducing a long alkyl chain and a short alkyl chain. Based on these results, the plant biomass, bagasse, cedar, and eucalyptus, which cannot normally form films, was able to form a thin film by substituting $[C_2mim][(MeO)(H)PO_2]$ for the hydroxy groups. In addition, these samples showed minimum film-forming temperatures close to that of bagasse acetate decanoate having a high substitution ratio.

The thermal decomposition temperature of the samples (the temperature when the residual

weight is 95%) was determined by the TGA under an air atmosphere. IL-bagasse, IL-cedar, and IL-eucalyptus showed thermal decomposition temperatures of 229, 234, and 232 °C, respectively (full TGA curves are shown in Fig. S6). The thermal decomposition temperature was higher than the minimum film-forming temperature (160, 140, and 140 °C), showing their possible use as thermoplastics. The thermal decomposition temperatures of untreated cedar and eucalyptus were 245 and 260 °C, which confirmed that the substitution of $[C_2mim][(MeO)(H)PO_2]$ decreased the thermal decomposition temperature by 11 and 28 °C, respectively. The decrease of the thermal decomposition temperature can be explained by decomposition and char formation temperature of phosphorus compounds at approximately 230 °C. The thermal decomposition temperature of IL-bagasse showed a minimal change after substitution with $[C_2mim][(MeO)(H)PO_2]$ (from 234 to 229 °C) because the thermal decomposition temperature of bagasse was near that of the phosphorus component. The same trend was observed when cellulose was derivatized (shifting from 313 to 230 °C). In contrast, the thermal decomposition temperature of bagasse acetate decanoate was 191 °C, indicating a higher thermal stability of the IL-biomass samples than that of the typical biomass thermoplastic.

The thermal properties of the polymers regarding the flame retardancy were measured (see Table 1). The residual weight of each sample was evaluated at 400 °C by a TGA under an air atmosphere as an index of the flame-retardancy[35] (see Fig. S6). Phosphoric acid-type flame retardants degrade at approximately 230 °C, as mentioned above, creating polyphosphate layers as char when

combusted and the layers block oxygen and heat.[35] Thus, the residual weight at over 230 °C, which is the char formation ability, is an indicator of the flame retardancy. The residual weights of IL-bagasse, IL-cedar, and IL-eucalyptus at 400 °C were 56, 57, and 55%, respectively. The residual weights of the untreated bagasse, cedar, and eucalyptus at 400 °C were 19, 26, and 21%, respectively. These suggest that the substitution of [C_2mim][(MeO)(H)PO_2] significantly increased the residual weight. On the other hand, the residual weight of bagasse acetate decanoate, a bagasse-based thermoplastic, was 22% and was approximately equal to that of the untreated biomass, indicating that it is not a flame-retardant material. However, the residual weight of bagasse acetate decanoate was higher than that of CP (12%) owing to the lignin. The flame retardancy of the IL-biomass samples was confirmed based on the TGA. The residual weight of a flame-retardant cellulose previously reported by Aoki et al. (i.e., a cellulose derivative prepared by adding a phosphoric acid-type flame retardant into CP using two steps, mentioned in the introduction section) was approximately 30% at 400 °C.[5] In addition, the residual weight of flame-retardant sawdust (Scots pine sapwood), although it is not a thermoplastic, was approximately 50% at 400 °C, which is prepared by substitution with diethyl chlorophosphite in pyridine[35], and the flame retardancy of the IL-biomass samples was equivalent. The flame-retardant effect of [C_2mim][(MeO)(H)PO_2] substitution was evaluated based on the weight percent gain (WPG). The WPG of the flame-retardant sawdust using diethyl chlorophosphite was 32%, and the residual weight was 52%. In our sample, the WPG of IL-bagasse was 39%, and the residual weight was 56%.

Based on these results, this method of substituting [C_2mim][(MeO)(H)PO_2] could sufficiently impart flame retardancy based on the WPG.

The residual weight of the IL-biomass samples was estimated from the residual weight of IL-cellulose, IL-xylan, and IL-lignin and the composition of the components in the biomass. The estimated residual weight was 58, 60, and 59% for IL-bagasse, IL-cedar, and IL-eucalyptus, respectively. The experimental values of the IL-biomass samples were similar to the estimated values (56, 57, and 55%, respectively). This indicates that the performance of [C_2mim][(MeO)(H)PO_2] in the IL-biomass samples was equivalent or more to that in the IL-pure biopolymers when considering the substitution ratios. These results may also indicate that the flame retardancy of the IL-biomass samples can be presumed. From these results, this method simultaneously imparted thermoplasticity and flame retardancy directly to the biomass, while maintaining hydroxy groups, and adding good flame retardancy equivalent to the IL-pure biopolymers, which was higher than the flame-retardant cellulose thermoplastic previously reported.[5] In addition, this method was applicable to a broad range of biomass species: grasses, softwoods, and hardwoods.

The TGA of each sample was also conducted under nitrogen (Fig. S7). The residual weights of IL-bagasse, IL-cedar, and IL-eucalyptus at 400 °C were 51, 55, 52%, respectively, and were approximately equal to those under air (56, 57, and 55%, respectively). In addition, van Krevelen reported a rough linear relationship between the limited oxygen index (LOI) and residual weight at

850 °C under nitrogen.[36] When this relation was applied to the samples, the corresponding LOI was approximately 0.31, 0.26, and 0.31 for IL-bagasse, IL-cedar, and IL-eucalyptus, respectively. Because materials with an LOI ≤ 0.26 are considered flammable materials[36], the IL-bagasse, and IL-eucalyptus samples are recognized as flame-retardant materials, while IL-cedar is marginal. The residual weight of bagasse acetate decanoate at 850 °C was 3%, and the corresponding LOI was 0.19; it suggests similar flammability to cellulose (LOI: 0.19)[36].

The samples were subjected to a brief fire test (Fig. 3 shows the photos of the IL-biomass samples after the fire test and Supplemental movies exhibit the burning behaviors). When the CP film contacted the fire of an alcohol lamp, it burned completely with forming a slight char and dripping. Bagasse acetate decanoate also burned completely with forming a slight char (Fig. S8). For bagasse acetate decanoate, there was no dripping, and the burning speed was slower. This difference could be because of the lignin, which is flame-retardant. For the IL-biomass samples, combustion started; however, char layers instantly formed, and the fire was self-extinguished. This was caused by the flame-retardant effect of $[C_2mim][(MeO)(H)PO_2]$ because the behaviors of the samples were consistent with that of phosphoric acid-type flame retardants. Therefore, thermoplasticity and firm flame retardancy were simultaneously imparted to grass, hardwood, and softwood by substituting $[C_2mim][(MeO)(H)PO_2]$.

The formed char layers on the samples were observed by scanning electron microscopy (Fig.

S9). The surface of the char layers of the IL-biomass samples was smooth, and there were numerous cavities of approximately 10–30 μm. Some of the cavities were independent, indicating foaming during the formation of the char layers. We have reported that $[C_2mim][(MeO)(H)PO_2]$ acted as an intumescent-type flame retardant for cellulose, xylan, and lignin.[6] In this research, it has also been confirmed that $[C_2mim][(MeO)(H)PO_2]$ acts as an intumescent-type flame retardant for the plant biomass. Conversely, the char layers of bagasse acetate decanoate were rough with no cavities of approximately 10–30 μm although very small continuous cavities (approximately 1 μm) were observed. Therefore, the introduction of $[C_2mim][(MeO)(H)PO_2]$ to the plant biomass caused generating cavities of approximately 10 μm separated by smooth char layers when flamed, which enhanced flame retardancy.

Thus, flame-retardant thermoplastics were developed from grass and wood biomasses with $[C_2mim][(MeO)(H)PO_2]$ at a low substitution ratio (≤ 13%). The ability to enable thermoplasticity and flame-retardancy at a low substitution was attributed to the functionalization by only a single species, $[C_2mim][(MeO)(H)PO_2]$. This method produced flame-retardant plastics without any extraction process of the single components, such as cellulose, and even pretreatment processes of the biomass, such as ball-milling. This is a new proposal for the reuse of fine biomass waste, such as bagasse and sawdust.

CONCLUSION

Thermoplasticity and flame retardancy were simultaneously imparted to plant biomass—bagasse, cedar, and eucalyptus—by dissolution into a $[C_2mim][(MeO)(H)PO_2]$/$[C_2mim]OAc$ mixture and precipitation. During dissolution, the hydroxy groups in the biomass were substituted with $[C_2mim][(MeO)(H)PO_2]$ using a substitution ratio of less than 14%, maintaining more than 86% of the hydroxy groups and thus demonstrating the potential for further functionalization. Furthermore, substitution with $[C_2mim][(MeO)(H)PO_2]$ prevented bleeding out. The minimum film-forming temperatures of IL-bagasse, IL-cedar, and IL-eucalyptus were 160, 140, and 140 °C, respectively, which were similar to the value of bagasse acetate decanoate (120 °C). The minimum film-forming temperatures of the IL-biomass samples were sufficiently lower than the thermal decomposition temperatures (229, 234, and 232 °C, respectively), and they could be used as thermoplastics. For a quantitative evaluation of the flame retardancy, the residual weights of the IL-biomass samples at 400 °C under air were investigated. The residual weights of IL-bagasse, IL-cedar, and IL-eucalyptus were 56, 57, and 55%, respectively. These were much larger than those of the raw biomasses (approximately 20%) and bagasse acetate decanoate (23%) and were equivalent to that of the flame-retardant (not thermoplastic) wood powder previously reported. In the burning test, while the CP and bagasse acetate decanoate were burned out with forming a slight char, the IL-biomass samples formed foamed char layers and then self-extinguished. The foamed char layers indicated that

[C_2mim][(MeO)(H)PO_2] acted as a thermoplasticizer and intumescent-type flame retardant, which is a very effective flame retardant.

CONFICT OF INTEREST

The authors declare no conflict of interest.

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Titles and legends to figures

Figure. 1 Reaction of $[C_2mim][(MeO)(H)PO_2]$ and components of biomass.

Figure. 2 Thin films of IL-bagasse (left), IL-cedar (center), and IL-eucalyptus (right) prepared by hot press.

Figure. 3 Thin films of IL-bagasse (left), IL-cedar (center), and IL-eucalyptus (right) after fire test.

Table. 1 Characteristics of biomass and biomass polymers before and after derivatization with $[C_2mim][(MeO)(H)PO_2]$, and CP and bagasse acetate decanoate.

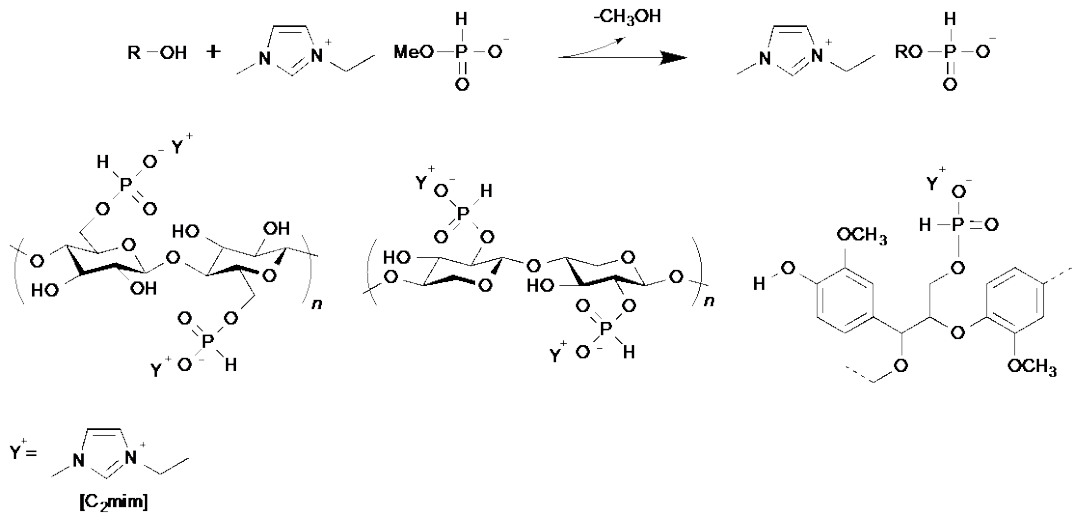

Figure. 1

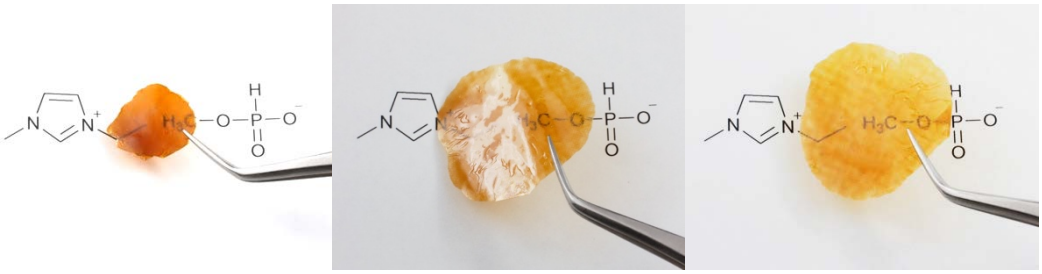

Figure. 2

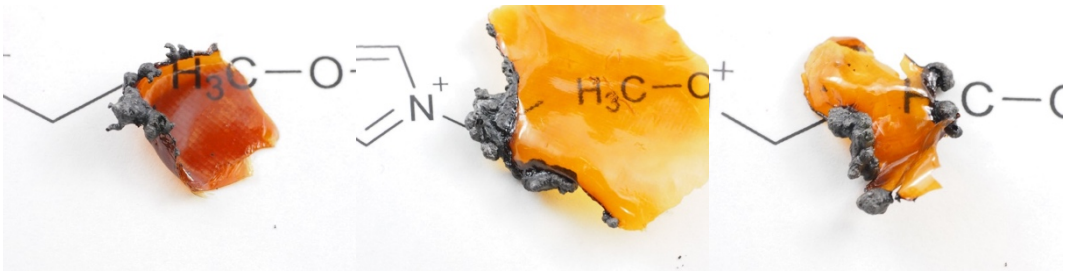

Figure. 3

Table. 1

	Substitution ratio in mol	Minimum film-forming temperature	Film character	Thermal decomposition temperature (5%)	Residual weight in air (at 400 °C)	Residual weight in N_2 (at 850 °C)	Char formation	Self-extinguishing property
Cellulose propionate	89%	160 °C	Soft	301 °C	12%	2%	Slightly formed	Completely burned
Cellulose	–	Not formed	–[b]	313 °C	11%	2%	–[b]	–[c]
IL-cellulose[a]	33%	100 °C	Soft	230 °C	52%	22%	✓(Foam)	✓
Xylan	–	Not formed	–[b]	235 °C	39%	3%	–[b]	–[c]
IL-xylan[a]	32%	140 °C	Soft	228 °C	48%	16%	✓(Foam)	✓
Lignin	–	Not formed	–[b]	256 °C	67%	47%	–[b]	–[c]
IL-lignin[a]	14%	180 °C	Hard	269 °C	74%	52%	✓(Foam)	✓
Bagasse acetate decanoate	97% (Acetate: 68% Decanoate: 29%)	120 °C	Soft	197 °C	25%	3%	Slightly formed	Completely burned
Bagasse	–	Not formed	–[b]	234 °C	19%	18%	–[b]	–[c]
IL-bagasse	13%	160 °C	Soft	229 °C	56%	33%	✓(Foam)	✓
Cedar	–	Not formed	–[b]	245 °C	26%	7%	–[b]	–[c]
IL-cedar	8%	140 °C	Soft	234 °C	57%	22%	✓(Foam)	✓
Eucalyptus	–	Not formed	–[b]	260 °C	21%	21%	–[b]	–[c]
IL-eucalyptus	10%	140 °C	Soft	232 °C	55%	33%	✓(Foam)	✓

[a]*The results are cited from R. Nishita et al., New. J. Chem. (Ref 6).*
[b]*Not evaluated because the samples did not form thin films.*
[c]*Not detected.*